Plutonium: The density-functional-theory point of view

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Plutonium: The density-functional-theory point of view

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Density-functional theory (DFT) is a remarkably successful tool for describing many metals throughout the Periodic Table. Here we present the results of this theory when applied to plutonium metal, the perhaps most complex and difficult-to-model metal of all. The fundamental product of DFT is the ground-state total energy. In the case of Pu, we show that DFT produces total energies that can predict the complex phase diagram accurately. Focusing on the δ phase, we show that DFT electronic structure is consistent with measured photoemission spectra. The observed non-magnetic state of δ-Pu could possibly be explained in DFT by spin moments, likely disordered, that are magnetically neutralized by anti-parallel aligned orbital moments. As an alternative to this non-magnetic model an extension of DFT with enhanced orbital polarization is presented in which magnetism can be suppressed.

Plutonium metal has many physical properties that are counterintuitive, puzzling, and intriguing. The perhaps most perplexing behaviors of Pu are displayed in its phase diagram. Notice in Figure 1 that it has as many as six condensed phases with stark contrasts in both atomic geometry and volume. At lower temperatures, Pu has very low symmetry atomic arrangements with small volumes (α and β monoclinic), then with increasing temperature it expands to higher symmetry (γ orthorhombic and δ cubic), followed by a volume collapse to lower symmetry (δ' tetragonal) before shrinking (ε cubic). These transitions take place in a limited temperature range suggesting that the phases compete closely with each other. Pu thus provides an extraordinary challenge for any theory that describes phase stability. In the literature one finds several models for Pu that unfortunately cannot be discussed in this short article.

The foundation of modern DFT took shape in the mid 60's with the famous papers by Hohenberg & Kohn, Kohn & Sham [1], for which Kohn received the Nobel Prize 1998. The theoretical framework has been implemented in gradually more accurate computer codes since its invention and is now the essential workhorse for first-principles calculations for materials. Although popular for describing many materials, its usefulness for plutonium may have escaped some of the non-specialists. Here we review some of the results and insights DFT gives us for Pu.

One important challenge for any theory is to evaluate its capability to reproduce or predict a phase diagram. The word "predict" is appropriate for DFT because in this theory no adjustable parameters are used to reproduce a wanted

(experimental) result. In Figure 2, we contrast DFT total energies for the six known phases of Pu [2] with the experimental phase diagram in Figure 1. Notice immediately that the theory rank the total energies in the order α, β, γ, δ, δ', and ε. This exact order is also found in the experimental phase diagram as a function of temperature. On a closer view, Figure 2 also reveals that the atomic volumes order exactly the same way as in Figure 1. Hence, DFT captures the main features of the very delicate and complex phase diagram of Pu. Because the various Pu phases are all stable at relatively low temperatures, the DFT total energy can approximately be corrected for temperature dependence of the vibrating atoms within a quasi-harmonic approach [3]. In Figure 3 we show the result of this correction by plotting the free energy as a function of temperature for the α, β, γ, and δ phase. The figure shows that temperature stabilizes these phases in accordance with the known phase diagram, displayed in Figure 1. This is a testament to the high quality of the DFT total energies. Comparable results have been published elsewhere [4].

Next, we focus on the important δ phase and relate the theoretical electronic structure with measured data. In Figure 4, we show calculated electronic density-of-states (DOS), that has been appropriately convoluted with instrumental and lifetime broadening [5], together with experimental photoemission data at two photon energies [5,6]. Clearly, these spectra are consistent with each other and DFT electronic structure appears to agree with experiments for δ-Pu. The DFT electronic structure is spin polarized with a resulting spin moment on each Pu atom. This would then seem to imply that DFT

predicts δ-Pu to be magnetic, something that has not been observed for pure Pu metal [7]. But for Pu nothing is simple or intuitive. Examining the DFT results for δ-Pu, it has been realized that (i) at temperature where it is stable, the spins are most likely disordered [8] and (ii) the orbital moment may perfectly cancel the spin moment making each Pu atom magnetically neutral [9]. If DFT is correct regarding (i) and (ii), then it make sense that no substantial evidence of magnetism in δ-Pu have been revealed.

If neither (i) nor (ii) is correct, then it is likely DFT is insufficient in modeling the nature of magnetism in Pu. It has been suggested that orbital correlations, in terms of spin-orbit coupling and orbital polarization, are much stronger than spin correlations and therefore the spin moments could appropriately be suppressed in a constrained DFT treatment [10]. In Figure 5 we show the total energies for calculations with the spin moment quenched (NM) in combination with spin-orbit coupling (SO) and orbital polarization (OP). Notice that addition of SO and OP both lowers the total energy substantially while simultaneously expanding the volume closer to the observed volume (V_δ). Allowing ferromagnetic spin polarization lowers the total energy further but does not improve on the equilibrium volume. It was further shown [10] that the main features (peak locations) of the DOS did not depend sensitively on the spin restriction. Therefore, one can argue that suppressing the spin moment, when the mentioned orbital correlations are accounted for, is a reasonable non-spin DFT model for δ-Pu. Another interesting observation [10], is that SO and OP substantially quench the spin moment (from 5 μ_B to about 3 μ_B).

The fact that spin-orbit coupling and orbital polarization have an intricate relationship to the spin moment was formally investigated in a recent publication [11]. By introducing two parameters, they were able to suppress the spin moment and accomplish a non-magnetic state in δ-Pu. Referring the details to their publication [11] it was discussed that the "conventional" OP correction, as used here and introduced by Brooks [12], could effectively be strengthened to possibly accomplish a similar non-magnetic state for δ-Pu. In Figure 6 we present calculations for δ-Pu done in the same fashion as the ones presented above (Figure 2) but with an amplification factor to the OP correction. A value equal to unity corresponds to our standard OP [12] while a value greater than unity attempts to model the full treatment with the introduced adjustable parameters [11]. Notice in Figure 6 that the ferromagnetic spin moment gradually approaches zero with increasing OP enhancement. At the same time, the atomic volume remains close to the observed value, whereas the bulk modulus apparently is becoming somewhat large. Thus, this approach, as well as the more complete treatment [11], represents a non-magnetic scheme for δ-Pu that, in contrast to DFT, relies upon one or more adjustable parameters. It remains to be seen if it can be applied also for the other phases, particularly the α phase, of Pu.

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Figure 1   The experimental phase diagram of Pu.

Figure 2   DFT total energies for the six known condensed phases of Pu.

Figure 3   Helmholtz free energies (see text).

Figure 4   Experimental δ-Pu photoemission spectra (125 eV [5] and 40.8 eV [6]), and theory [5].

Figure 5   DFT total energies, non-magnetic (NM, zero spin) and ferromagnetic (FM), for δ-Pu. Spin-orbit interaction and orbital polarization are denoted SO and OP, respectively.

Figure 6   Spin (S), atomic volume (V), and bulk modulus (B) as functions of orbital-polarization enhancement factor. Dashed horizontal lines denote the measured values.
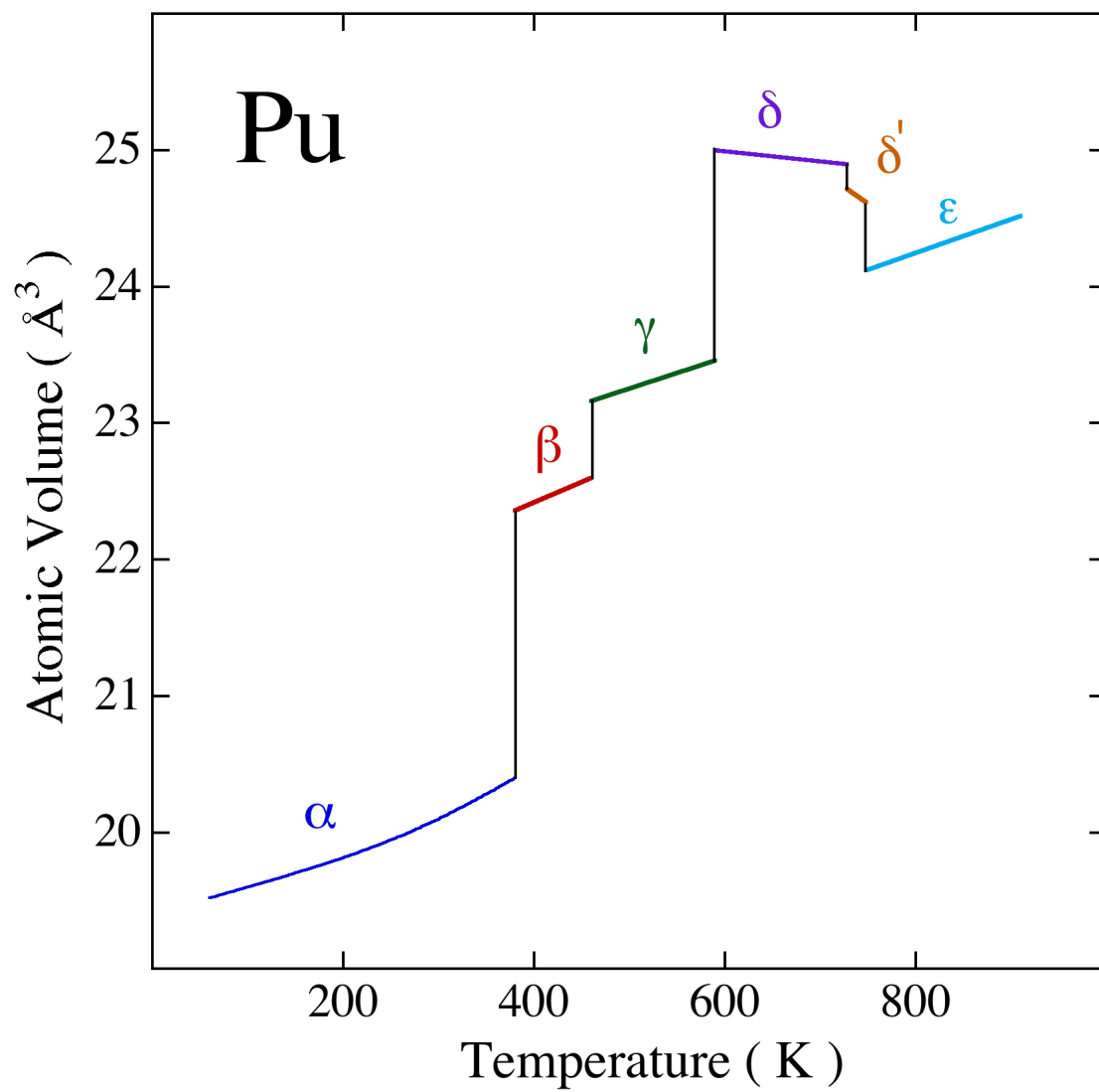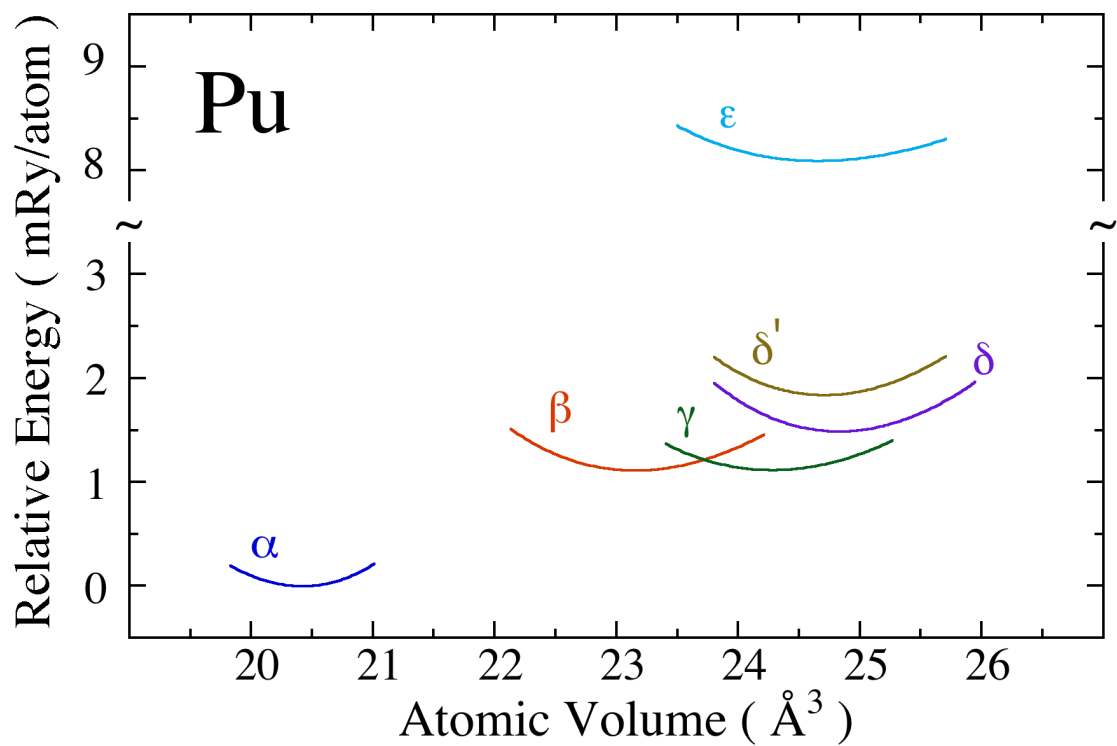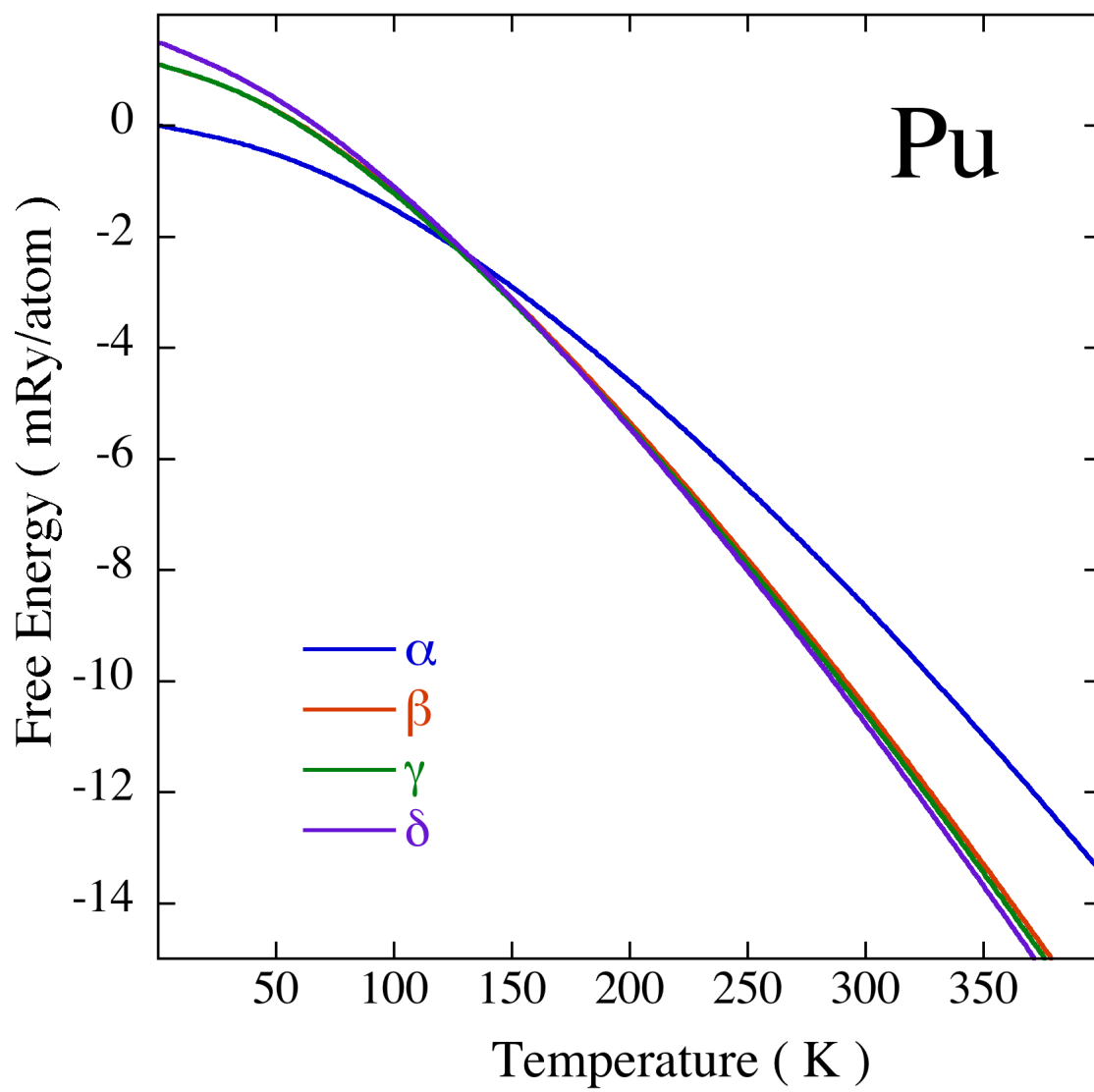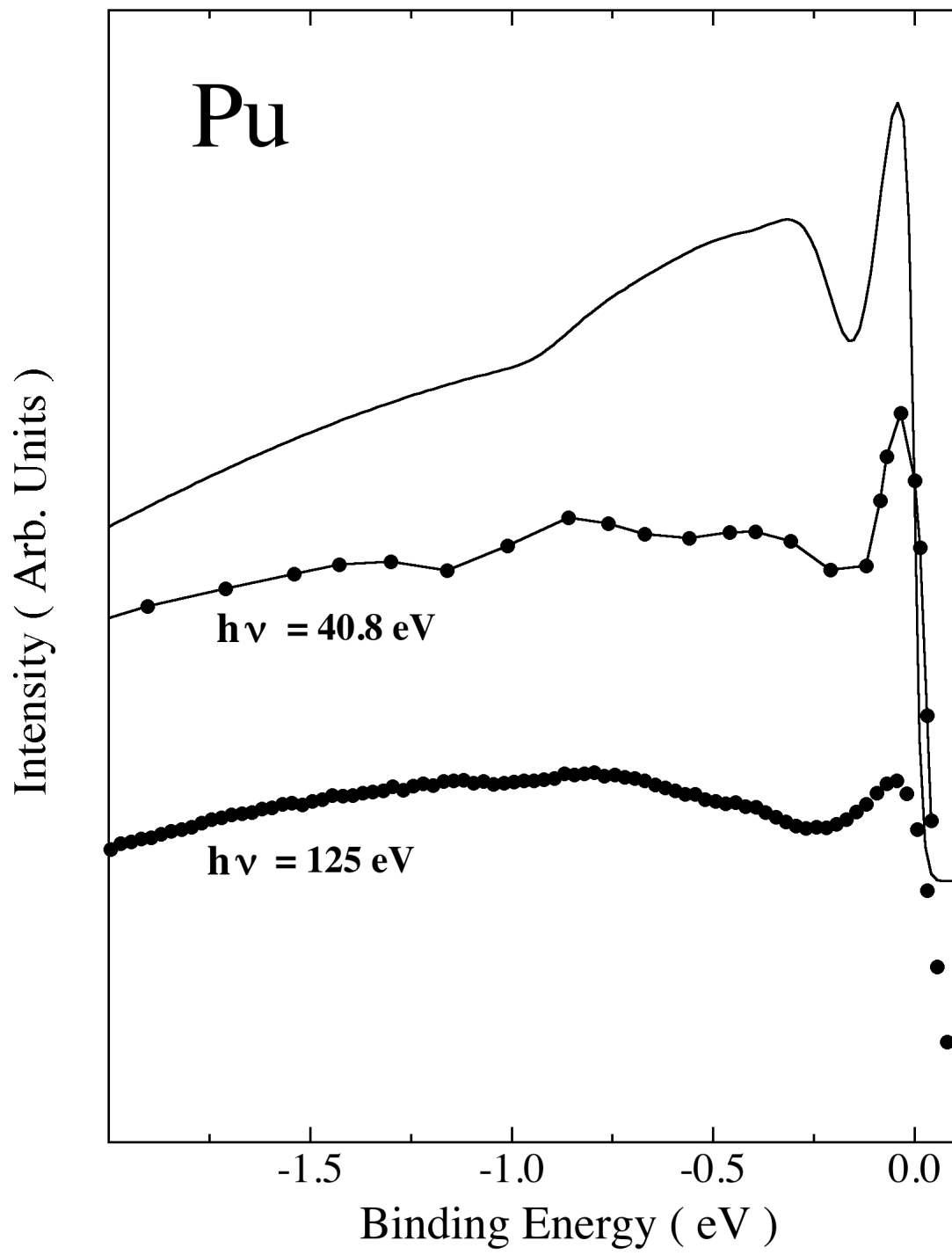
Figure 1

Figure 2

Figure 3

Figure 4

Pu

Intensity (Arb. Units)

hν = 40.8 eV

hν = 125 eV

Binding Energy (eV)

-1.5   -1.0   -0.5   0.0

Figure 5

Figure 6